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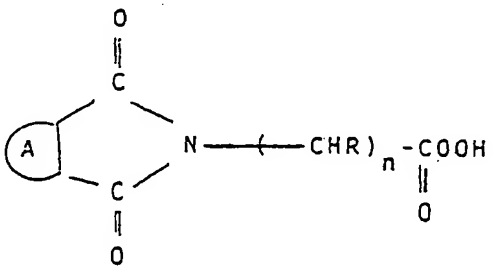
(54) Novel imido-aromatic percarboxylic acids.

(57) There are described novel imido-aromatic (poly)percarboxylic acids of the formula (I):



(I)

wherein: A represents an optionally substituted benzene or naphthalene ring, R is hydrogen, lower alkyl, COOH or COOOH and n is an integer of from 1 to 5.

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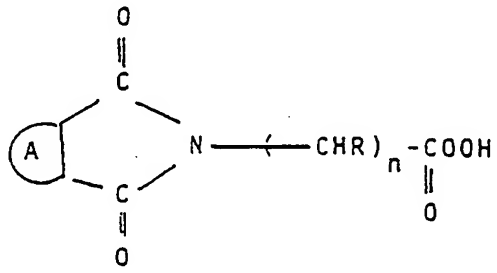
NOVEL IMIDO-AROMATIC PERCARBOXYLIC ACIDS

The present invention relates to new (poly)percarboxylic acids, which may be referred to as imido-aromatic (poly)percarboxylic acids, and to a process for the preparation thereof.

In particular, the present invention relates to imido-aromatic (poly)percarboxylic acids having the formula (I):



(I)

wherein: A represents an optionally substituted benzene or naphthalene ring, the group or groups R, which may be the same or different from one another, represent hydrogen, an optionally substituted alkyl group, COOH or COOOH and n is an integer of from 1 to 5, preferably from 1 to 3.

Preferably, the (linear or branched) alkyl groups R have 1 to 5 carbon atoms. Examples of C_{1-5} alkyl groups are methyl, ethyl, n- and i-propyl, n-, i-, sek.- and tert.-butyl and pentyl. Said groups may optionally be substituted, e.g. with one or more (preferably 1 to 3) radicals selected from C_{1-5} alkoxy (e.g. methoxy and ethoxy), OH, COOH or COOOH, $COOR'$ (R' = C_{1-5} alkyl), NO_2 and halogen (e.g. F, Cl and Br). Examples of such groups are $-CH_2OCH_3$, $-CH_2OC_2H_5$, CH_2OH, $-CH_2COOH$, $-CH_2COOOH$, $-CH_2H_2COOH$, $-CH_2CH_2COOOH$, CH_2Cl, $-CH_2F$, CF_3 and $-CH_2COOC_2H_5$.

Likewise, the group A may carry one or more (up to 4 and preferably 1 or 2) substituents. Said substituents may be selected, e.g. from the ones recited above as substituents for the alkyl groups R and, additionally, from C_{1-5} alkyl groups. Particularly preferred substituents are COOH and COOOH radicals. Preferred (optional) substituents for the C_{1-5} alkyl groups R' are the same as those already mentioned above in connection with the groups R.

A particularly preferred meaning of R is hydrogen.

The imido-aromatic (poly)percarboxylic acids having the above formula (I) are novel compounds, and constitute a new class of products that is highly interesting from an industrial point of view.

In fact, they may find general use, similar to that already known for peroxyacids, in the field of plastics, as polymerization initiators and, in particular, as oxidizing agents in epoxidation and hydroxylation, and in many other oxidation processes in the field of fine chemicals.

Particularly, the imido-aromatic (poly)percarboxylic acids having the above formula (I) are particularly suitable as effective bleaching agents in detergent formulations.

In the past, organic peracids have encountered increasing interest in the industrial field, among others due to their excellent properties as bleaching agents in formulations for medium-low temperature washing, and the resulting saving of energy.

Therefore, there is a large number of publications concerned with organic peracid compounds endowed with the required properties of sufficient bleaching activity, and, in particular, thermal stability, the latter characteristics being essential for an industrial application and a widespread use of such compounds.

Therefore many organic straight-chain or cyclic mono- or dipercarboxylic acids are known and used, e.g. in detergent compositions.

Examples of already described percarboxylic acids are diperdodecanedioic acid, monoperphthalic acid, diperazelaic acid, substituted diperglutaric and adipic acids, etc.

Therefore, one object of the present invention is to provide, as per se novel compounds, the imido-aromatic (poly)percarboxylic acids having the above formula (I).

Another object is to provide a simple, inexpensive process for the preparation of the above percarboxylic acids of formula (I).

A further object is the use of imido-aromatic percarboxylic acids of formula (I) as bleaching agents in detergent formulations, particularly those intended for low-medium temperature use.

These, and still other objects which will become even clearer for those skilled in the art from the following description, are achieved, according to the present invention, by the imido-aromatic (poly)-percarboxylic acids of the above formula (I), and by the corresponding preparation process, which is characterized in that a substrate selected from imido-aromatic (poly)carboxylic acids and anhydrides thereof having a structure corresponding to the desired percarboxylic acid of formula (I), is reacted with concentrated H_2O_2, in a reaction medium selected from concentrated H_2SO_4 and CH_3SO_3H or in an alkaline medium, and in that the percarboxylic acid (I) is then separated from the reaction mixture by conventional and known techniques.

In this manner the percarboxylic acids of formula (I) may be obtained, generally as stable solids.

Particularly, preferred compounds of formula (I) according to the present invention are phthalimido-peracetic acid, 3- phthalimido-perpropionic acid 4 -phthalimido-perbutyric acid, 2-phthalimido-di-perglutaric acid, 2-phthalimido-dipersuccinc acid, 3-phthalimido-perbutyric acid, 2-phthalimido-perpropionic acid, 3-phthalimido-di-peradipic acid, naphthalimido-peracetic acid, 2-phthalimido-mono-persuccinic acid and 4-(4-percarboxy)-phthalimido-perbutyric acid.

As stated above said peracids may be obtained according to substantially conventional methods, by the reaction of a substrate selected from the imido-aromatic (poly)carboxylic acids of a structure corresponding to the desired peracids of formula (I) with H_2O_2 in sulphuric or methanesulphonic acid and by subsequent separation and so forth, according to known techniques, or by working in an alkaline medium, according to known methods, starting from the corresponding anhydrides.

When at least one -(CHR)- residue present in the formula of the starting substrate comprises a carboxylic group it is possible to prepare the corresponding peracid of formula (I) by using the corresponding anhydride.

In this case, depending on the reaction conditions (acidic or alkaline medium and so forth) di- or mono-peracids, i.e. compounds containing two percarboxylic acid groups or one percarboxylic acid group and one carboxylic acid group may selectively be obtained.

According to a preferred procedure, the percarboxylation reaction of the acid or poly-acid used as the starting substrate, is carried out by gradually adding H_2O_2, having a concentration of from about 70% to about 90% by weight, to a solution of the acid in concentrated H_2SO_4, or in CH_3SO_3H, maintaining the reaction temperature throughout the reaction within the range of from about 15° to about 50° C, depending on the reactivity of the substrate.

The amount of H_2SO_4 or CH_3SO_3H, determined at a concentration of 100%, preferably is from 3 to 20 moles per mole of substrate, particularly from about 4 to 14 moles per mole of substrate.

The hydrogen peroxide preferably is used in amounts in excess of that of the substrate. Generally the amounts range from about 2 to 6 moles H_2O_2 per mole of substrate, particularly from about 2.2 to 5 moles per mole of substrate, depending on the COOH groups to be percarboxylated.

The reaction time depends on the nature of the substrate, on the reaction temperature, and the total H_2SO_4/H_2O or $CH_3\ SO_3H/H_2O$ molar ratio at the end of the reaction. Said ratio preferably ranges from about 1 to 6 and, particularly, from about 1.6 to 4, by choosing suitable values for the various parameters involved.

Reaction times of from about 30 minutes to 2 hours are generally required.

The separation of the imido-aromatic (poly)percarboxylic acid of formula (I) may be carried out according to conventional techniques, such as e.g. filtration of the solid precipitate obtained after treatment of the reaction mixture with an ammonium sulfate solution, solvent extraction etc.

The imido-aromatic (poly)percarboxylic acids of formula I may thus be obtained in the form of crystalline solids.

The substrates, used as the starting materials, are per se known compounds, or can be prepared according to conventional methods. Examples of suitable substrates are phthalimido-acetic acid, 3-phthalimido-propionic acid, 4-phthalimido-butyric acid, 2-phthalimido-glutaric acid and the corresponding anhydride, 2-phthalimido-succinic acid and the corres ponding anhydride, 3-phthalimido-butyric acid, 2-phthalimido-propionic acid, methyl half-ester of 2-phthalimido-glutaric acid, 3-phthalimido-adipic acid, naphthalimido-acetic acid, phthaloyl serine, 4-(4-carboxy)-pthalimido-butyric acid, and so forth, from which the above preferred peracids of formula (I) are obtained.

The percarboxylic acid products of formula (I) are usually solid at room temperature.

According to the present invention, they may be used in detergent formulations, e.g. granular formulations, as bleaching agents in solution over a wide temperature range, e.g. of from 20° C to 90° C.

Therefore, the imido-aromatic peracids of the present invention may be used as bleaching agents either as such, e.g. separate from the detergent composition, or, preferably, associated to and incorporated into conventional detergent compositions which are used within the above defined temperature range and

contain other components and/or additives, such as e.g. builders, surfactants, soaps, zeolites, hydrotropic agents, corrosion inhibitors, enzymes, optical brighteners, stabilizers, other brightener compounds etc.

Preferably, the working temperature ranges from room temperature to about 65 °C.

The preparation and use of the compositions and the corresponding formulations are carried out according to the described and/or conventional techniques.

The imido-aromatic peracids of the present invention may be used in combination with solid and liquid detergent compositions, and/or in the presence of other bleaching (peroxy) compounds.

Further, the present imido-aromatic peracids may be subjected to a known phlegmatization process

The following examples serve to illustrate the present invention without being a limitation of the scope thereof.

The products prepared in the examples were characterized by elemental analysis, determination of their content of active oxygen (by iodometric titration), and by Fourier Transform Infrared Spectroscopy (FT-IR).

Example 1

330 g (3.434 mole) of methanesulphonic acid were placed in a beaker equipped with stirrer, thermometer and external bath.

The internal temperature was increased to 25 °C and 55 g (0.268 mole) of phthalimido-acetic acid were added under stirring within 15 minutes.

The temperature was then lowered to 10 °C and 44 g of H_2O_2 (70%, 0.906 mole) were gradually added under stirring, at a rate such as to maintain the temperature below 15 °C.

Stirring was continued at 15 °C for 1.5 hours.

At the end, the reaction mixture was poured into 600 ml of 20% $(NH_4)_2SO_4$, maintained under stirring at 5 °C.

Stirring was continued for 15 minutes at a temperature between 5 °-10 °C.

The solid product was filtered under vacuum over a porous septum. The thus obtained product was suspended in 400 ml of 8% Na_2SO_4 and neutralized (pH 6) by addition of a 15% Na_2CO_3 solution.

The resulting solid was then filtered, washed with ice water (100 ml), wiped and dried on a porous plate in a $CaCl_2$-drier under vacuum (2 mm Hg) at room temperature.

There were obtained 58 g of substantially pure phthalimidoperacetic acid. Yield: 97%.

The product may be recrystallized by dissolving it in ethyl acetate and by adding petroleum ether until the solution becomes turpid.

Elemental Analysis:

Calculated for $C_{10}H_7O_5N$: C: 54.30%; H: 3.19%; N: 6.33%; O (active): 7.23%.
Found: C: 54.32%; H: 3.33%; N: 6.57%; O (active) : 7.2%.
Melting Point: 118 °C (with decomposition).

Example 2

28 g (0.274 mole) of 96% H_2SO_4 were introduced into a beaker equipped with stirrer, thermometer and external bath.

The inside temperature was brought to 25 °C and 11.7 g (0.0534 mole) of 3-phthalimido-propionic acid were added under stirring within 15 minutes.

The temperature was lowered to 10 °C and 5.2 g H_2O_2 (70%, 0.107 mole) were gradually added under stirring, at a rate such as to maintain the temperature below 15 °C.

The stirring was continued at 15 °C for 1.5 hours. At the end, the reaction mixture was poured into 80 ml of 20% $(NH_4)_2SO_4$, maintained under stirring at 5 °C. Stirring was continued for 15 minutes at a temperature between 5 and 10 °C.

The solid product was filtered under vacuum over a porous septum.

The thus obtained product was suspended in 50 ml of 8% Na_2SO_4 and neutralized by adding (pH 6) 15% Na_2CO_3. The resulting solid was again filtered, washed with 20 ml of ice water, wiped and dried on a porous plate in a $CaCl_2$-drier under vacuum (2 mm Hg) at room temperature.

11.3 g of substantially pure 3-phthalimido-perpropionic acid were thus obtained. Yield: 90%.
The product may be recrystallized as described in Example 1.

Elemental Analysis:

Calculated for $C_{11}H_9O_5N$: C: 56.17%; H: 3.85%; N: 5.95%; O (active): 6.80%.
Found: C: 56.83%; H: 4.01%; N: 6.10%; O (active): 6.79%.
Melting point: 91 °C (with decomposition).

Example 3

The procedure of Example 2 was repeated, replacing 3-phthalimido-propionic acid by 4-phthalimido-butyric acid (15 g; 0.0643 mole) and using 30 g of 96% H_2SO_4 (0.294 mole) and 7 g of H_2O_2 (70%, 0.144 mole) and prolonging the reaction time to 2 hours.

14.5 g of substantially pure 4-phthalimido-perbutyric acid were obtained. Yield: 90%.
The product may be recrystallized as described in Example 1.

Elemental Analysis:

Calculated for $C_{12}H_{11}O_5N$: C: 57.83%; H: 4.45%; N: 5.62%; O (active): 6.42%.
Found: C: 57.98%; H: 4.52%; 5.69%; O (active): 6.41%.
Melting point : 103 °C (with decomposition).

Example 4

The procedure of Example 1 was repeated, replacing phthalimido-acetic acid by 2-phthalimido-glutaric acid (6 g; 0.0216 mole) and using 28 g (0.291 mole) of methanesulphonic acid and 3.5 g of H_2O_2 (85%, 0.0875 mole).

At the end, 15 ml of 40% $(NH_4)_2SO_4$ were gradually added to the reaction mixture, cooled to 0 °C, at a rate such that the temperature was maintained between 0 and 5 °C.

The resulting mixture was extracted with Et_2O (6 x 30 ml).

The ether extract was washed with 30 ml of 40% $(NH_4)_2SO_4$, dried over anhydrous Na_2SO_4, filtered and evaporated.

An oil was obtained which was dissolved in Et_2O (20 ml) and precipitated, as a solid, by adding petroleum ether (40 ml) and maintaining the mixture under agitation up to complete solidification.

After filtration, 5.8 g of 2-phthalimido-diperglutaric acid (95%) were obtained. Yield: 82%.
The product was recrystallized as described in Example 1.

Elemental Analysis:

Calculated for $C_{13}H_{11}O_8N$: C:50.49%; H: 3.58%; N: 4.53%; O (active): 10.34%.
Found: C: 49.96%; H: 3.75%; N:4.70%; O (active): 10.33%.
Melting point : 112 °C (with decomposition).

Example 5

The procedure of Example 4 was repeated, replacing 2-phthalimido-glutaric acid by 2-phthalimido-succinic acid (5 g; 0.019 mole), using 20 g (0.208 mole) of methanesulphonic acid, 3.8 g (0.095 mole) of 85% H_2O_2 and extending the reaction time to 2 hours.

At the end, 80 ml of a 40% $(NH_4)_2SO_4$ solution were gradually added to the reaction mixture, cooled to 0 °C, at a rate such that the temperature was maintained between 0 and 5 °C.

Stirring was continued for 15 minutes at 0-5 °C.

The procedure described in Example 2 was then followed.
4 g of substantially pure 2-phthalimido-dipersuccinic acid were obtained. Yield: 71%.
The product may be recrystallized as described in Example 1.

Elemental Analysis:

Calculated for $C_{12}H_9O_8N$: C: 48.82%; H: 3.07%; N: 4.74%; O (active): 10.84%.
Found: C: 48.44%; H: 3.22%; N: 4.88%; O (active) : 10.82%.
Melting point: 131 °C (with decomposition).

Example 6

The procedure of Example 5 was repeated, replacing 2-phthalimido-succinic acid by 2-phthalimido-succinic anhydride (2 g; 0.0082 mole), using 10 g (0.104 mole) of methanesulphonic acid and 1.3 g (0.0325 mole) of 85% H_2O_2, and reducing the reaction time to 1.5 hours.

At the end, 60 ml of a 20% $(NH_4)_2SO_4$ solution were gradually added to the reaction mixture, cooled to 0 °C, at a rate such that the temperature was maintained between 0 and 5 °C.

The resulting mixture was extracted with EtOAc/Et_2O 1:2 (2 x 30 ml). The organic extract was washed with 20 ml of a 20% $(NH_4)_2SO_4$ solution, dried over anhydrous Na_2SO_4, filtered and evaporated under vacuum.

1.8 g of 2-phthalimido-dipersuccinic acid (95%) were obtained. O (active) found: 10.3%; O (active) calculated for $C_{12}H_9O_8N$: 10.84%.

Example 7

5 g of a 17.4% Na_2CO_3 solution were placed in a 50 ml beaker. The internal temperature was brought to 5 °C and 0.8 g of 85% H_2O_2 and 0.04 g of $MgSO_4$. 7 H_2O were introduced.

While maintaining a temperature of 5 °C, 2 g of 2-phthalimido-succinic anhydride (0.0082 mole) were successively and rapidly added.

The internal temperature was allowed to gradually increase to 20 °C by continuing stirring for 30 minutes.

30 ml of ethyl ether and 4.2 g of 20% H_2SO_4 were then added. The ether layer was successively separated, washed with a 40% $(NH_4)_2SO_4$ solution (2 x 20 ml) and dried over anhydrous Na_2SO_4. Then, after the filtration of the sulphate, the peracid was precipitated by adding 30 ml of petroleum ether and stirring the mixture at room temperature for 30 minutes. The peracid was filtered and dried under vacuum at room temperature.

1.5 g of 2-phthalimido-mono-persuccinic acid (63%) were obtained.
O (active) found: 3.6%; O (active) calculated for $C_{12}H_9NO_7$: 5.73%.

Example 8

1.5 g of 85% H_2O_2 (0.0375 mole) were added, under stirring at 15-20 °C, to 2 g of a suspension of 4-(4-carboxy)-phthalimido-butyric acid (0.0072 mole) in 12 g (0.125 mole) of methanesulphonic acid.

Stirring was continued for 2 hours at 15 °C.

The reaction product was then poured in 40 ml of a 40% $(NH_4)_2SO_4$ solution maintained at 5 °C and, after 15 minutes of stirring, the separated solid product was filtered. The solid was then neutralized (pH 6) by suspending it in a 8% Na_2SO_4 solution and by adding a 15% Na_2CO_3 solution.

The resulting solid was again filtered, washed with ice water (30 ml) and dried on a porous plate in a $CaCl_2$ drier.

The product may be recrystallized by dissolving it in ethyl acetate at room temperature and precipitation thereof by adding petroleum ether.

There were thus obtained 2 g of substantially pure 4-(4-percarboxy)-phthalimido-perbutyric acid. Yield:

90%.

Elemental Analysis:

Calculated for $C_{13}H_{11}O_8N$: C: 50.49%; H: 3.58%; N: 4.53%; O (active): 10.35%.
Found: C: 50.04%; H: 3.75%; N: 4.48%; O (active): 10.34%.
Melting point: 109° C (with decomposition).

Examples 9-12 (Application examples)

Bleaching tests were carried out with the same concentrations of active oxygen in the bleaching solution, and by using the imido-aromatic peracids of the present invention, shown in the following table I, as compared to H.48 peracid (Mg salt of monoperphthalic acid), manufactured by INTEROX Chemical Ltd. London, U.K. for detergent compositions.

All tests were carried out at a constant temperature of 60° C, with an initial concentration of total active oxygen in the bleach (equal for all products) of 200 mg/l.

Procedure

For each test, 500 ml of deionized water, contained in a 1,000 ml flask equipped with a condenser, were heated to a temperature of 60° C and adjusted to a pH value of 9.5 (with a few drops of NaOH solution). Then, the bleaching product was added, under stirring, in the amounts given in the following Table 3, and immediately thereafter, two cotton specimens (10 x 10 cm) stained in standard manner by red wine at the EMPA INSTITUTE of St.Gallen (Switzerland), and marked with the "EMPA 114" mark, were added.

The system was subsequently stirred for 60 minutes and, at the end of this time, the specimens, rinsed under running water, were dried and ironed, and were then subjected to the evaluation of the bleaching effect by determining the degree of whiteness by reflectometry. The results are reported in the following Table I, expressed as % Bleaching as defined in the following:

$$\% \text{ Bleaching} = \frac{A - B}{C - B} \times 100$$

wherein:
A = degree of whiteness (%) of the specimen bleached after the test;
B = degree of whiteness (%) of the specimen before the test;
C = degree of whiteness (%) of the completely bleached specimen.
The degree of whiteness was measured by means of an Elrepho Zeiss Reflectometer using a filter N.6λ = 464 mm) and assuming MgO = 100% of whiteness.

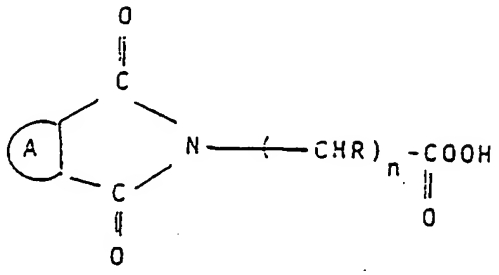
The obtained results show that the peracids of the present invention have a bleaching power which may be compared to that of H.48 and in some cases is even higher.

Table I

COMPOUND	Amounts used in the test (grams)	Initial concentration of total active oxygen (mg/l)	% Bleaching
- Example 1 (titer: 7.2% of active oxygen)	1.46	200	83.6
- Example 2 (titer: 6.79% of active oxygen)	1.47	200	83.0
- Example 3 (titer: 6.41% of active oxygen)	1.56	200	79.4
- Example 4 (titer: 9.81% of active oxygen)	1.02	200	74.0
- Example 5 (titer: 10.82% of active oxygen)	0.924	200	75.0
- H 48 (titer: 5.5% of active oxygen)	1.86	200	75.1

Claims

1. Imido-aromatic (poly)percarboxylic acids having the formula:



(I)

wherein A represents an optionally substituted benzene or naphthalene ring, the groups R, which may be the same or different from each other, represent hydrogen, an optionally substituted alkyl group, COOH or COOOH and n is an integer of from 1 to 5.

2. Imido-aromatic (poly)percarboxylic acids according to claim 1, wherein the group(s) R are selected from straight or branched alkyl groups containing from 1 to 5 carbon atoms, and preferably are hydrogen atoms.

3. Imido-aromatic (poly)percarboxylic acids according to the preceding claims, wherein said R alkyl group or groups may in turn be substituted by one or more, optionally different substituents selected from OH, NO_2 and lower alkoxy.

4. Imido-aromatic poly(percarboxylic acids) according to any one of the preceding claims wherein A is substituted by at least one CO_2H or CO_3H radical.

5. Imido-aromatic (poly)percarboxylic acids according to any one of the preceding claims, namely phthalimido-peracetic acid, 3-phthalimido-perpropionic acid, 4-phthalimido-perbutyric acid,2-phthalimido-diperglutaric acid, 2-phthalimido-dipersuccinic acid, 2-phthalimido-monopersuccinic acid, 3-phthalimido-perbutyric acid, 2-phthalimido-perpropionic acid, 3-phthalimido-diperadipic acid, naphthalimido-peracetic acid and 4-(4-percarboxy)-phthalimido-perbutyric acid.

6. Process for preparing the (poly)percarboxylic acids according to claim 1, characterized in that a substrate selected from imido-aromatic (poly)carboxylic acids, or anhydrides thereof, corresponding to the desired percarboxylic acid of formula (I), is reacted with concentrated H_2O_2 in a medium selected from concentrated H_2SO_4 and CH_3SO_3H or in an alkaline medium.

7. Use of the imido-aromatic (poly)percarboxylic acids of formula (I) as bleaching agents, either alone or in liquid or solid detergent formulations containing other components and/or additives, such as builders, surfactants, soaps, zeolites, hydrotropic agents, corrosion inhibitors, enzymes, optical bleaching agents, stabilizers and other peroxy compounds.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 10 1002

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	JOURNAL OF THE CHEMICAL SOCIETY, 1962, Part III, pages 2837-4264, The Chemical Society, London, GB; K. BALENOVIC et al.: "Preparation of some peroxy-acids derived from optically active amino-acids" * Whole article * ---	1	C 07 D 209/48 C 07 D 209/66 D 06 L 3/02 C 11 D 3/395
A	EP-A-0 170 386 (PROCTER & GAMBLE) * Claim 1 * -----	1,7	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 07 D 209/00
D 06 L 3/00
C 11 D 3/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21-04-1989	CASADO Y MARTIN DE MERCA

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)